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Preparation of ^{26}Al, ^{59}Ni, ^{44}Ti, ^{53}Mn and ^{60}Fe from a proton irradiated copper beam dump

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Abstract The station for pions cancer therapy was operated at PSI from 1980 to 1992. After a cooling time of 12 years it's made of copper beam dump was cut and samples were taken for analytical purposes. The sampling collected about 500 g of high active copper chips that can be used for separation of exotic radionuclides. The analyses by gamma spectrometry, LSC and AMS showed main nuclides present to be ^{60}Co, ^{54}Mn, ^{22}Na, ^{65}Zn, ^{26}Al, ^{53}Mn, ^{59}Ni, ^{63}Ni, ^{55}Fe and ^{60}Fe and ^{44}Ti with a daughter nuclide ^{44}Sc. In the frame of ERAWAST project a procedure combining selective precipitation and ion exchange for the separation of the rare radionuclides from the copper beam dump was developed. The proposed separation procedure is easy for remote controlled implementation in a hot cell. The ion exchange separation of Ni, Al, Mg, Ti and Fe was complete and high decontamination factors for copper and cobalt were achieved. Based on the developed procedure a remotely controlled system for separation of exotic radionuclides from the copper chips was set up. The full scale system was installed in a hot cell where high activity levels can be handled. In order to evaluate the reliability and functionality of the system extensive tests have been done. During the test period 13.86 g in total of the proton irradiated copper beam dump were processed for separation of ^{26}Al, ^{59}Ni, ^{53}Mn, ^{44}Ti and ^{60}Fe. The results showed that the system was operational and the radionuclide separation was selective with high chemical yield. The procedure manages as well the generated liquid wastes containing high level of ^{60}Co activity.

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Introduction

Exotic radionuclides with long half-lives, such as ^{26}Al (7.2×10^5 years), ^{53}Mn (3.7×10^6 years), ^{44}Ti (60.4 years) [1] and ^{60}Fe ($2.6\ 10^6$ years) [2] are of great interest in research domains such as astrophysics, nuclear structure, nuclear medicine, geophysics and fundamental nuclear physics. Conventional techniques for commercial production of radionuclides approach their limitations. Consequently, alternative production possibilities through cooperation between different branches of science at large basic-physics-oriented facilities are presently being explored. A promising possibility is the exploitation of particle accelerator components that have, over many years, been exposed to high-intensity radiation. One such facility is the 590 MeV ring cyclotron at PSI. With a beam current of up to 1.8 mA, this cyclotron is the most powerful accelerators in Europe, and is an excellent candidate to provide the long-lived radionuclides that are needed [3].

Extensive work has been done at PSI in order to characterize the existing activated material that could serve as a source of exotic radionuclides. The first and most completely analyzed such a material is a copper beam dump, which was in operation for 12 years at the former "Bio-Medical-Area" (BMA), there the patients were treated for cancer with negative pions produced in a beryllium target hit by 590 MeV protons. The results form the analytical procedures demonstrated that the cooper beam dump could serve as a valuable source for production of rare radionuclides such as ^{26}Al, ^{36}Cl, ^{32}Si, ^{59}Ni, ^{53}Mn, ^{44}Ti and ^{60}Fe. Therefore, based on the analytical results, a special

research and development program has been started at PSI objecting on specific preparative extraction of long lived radioisotopes (ERAWAST—exotic radionuclides from accelerator waste for science and technology) [4, 5].

In the present paper, we are going to discuss the radiochemical separation procedure developed for selective separation of ^{26}Al, ^{59}Ni, ^{53}Mn, ^{44}Ti and ^{60}Fe from proton irradiated copper beam dump, as well as a hot-cell installed and remote controlled separation system.

Experimental

Instrumentation and reagents

Packard TriCarb 2250 CA instrument was used for liquid scintillation counting (LSC). Gamma spectrometry was performed with high purity germanium detectors (160 cm^3 sensitive volume, 35% efficiency and FWHM 1.75 keV at energy 1,332 keV). The samples from cold experiments were analyzed by ICP-OES (Varian Vista pro AX). The transport and switching of the fluids was performed by *Ismatec REGLO Digital* pumps and *Neptune Research* solenoid valves. The remote control of the valves and pumps as well as measurements of radioactivity and temperatures was based on a *National Instruments* control and measurement unit cDAQ-9172.

All the chemicals were of analytical grade if not otherwise stated and Milli Q water was used. The material that served for the separation of rare radionuclides is described in details elsewhere [5]. The expected radionuclide inventory of the collected copper sample (500 g) is listed in the Table 1 [5].

All the radionuclides can be separated without addition of stable carrier, but some of them contain other long lived isotopes of the same element, for example ^{63} Ni and ^{55}Fe.

Radiochemical separation procedure

The separation of carrier free exotic radionuclides from the copper target is a challenging task. The differences of the chemical properties of the elements require combination of various separation steps e.g. precipitation, extraction, ion-exchange, in order to obtain proper separation. From the other side the high ^{60}Co gamma activity present in the sample material imposes the need of a separation procedure that could be easily implemented in a remote controlled system installed in a hot-cell.

Table 1 Radionuclides inventory of the copper sample—500 g

Radionuclide	Activity	Number of atoms
^{26}Al	7 kBq	10^{17}
^{44}Ti	100 MBq	10^{18}
^{53}Mn	500 kBq	10^{19}
^{59}Ni	8 MBq	10^{19}
^{60}Fe	5 kBq	10^{17}
^{60}Co	5 GBq	–

For the radiochemical separations we chose a combination of a selective precipitation of the copper matrix followed by ion exchange chromatography.

Dowex 1 × 8—HCl and Dowex 50 × 8—HCl were used to obtain a selective and a high yield separation [6, 7]. The copper exhibits a relatively high distribution coefficient in the system Dowex 1 × 8—HCl over a broad range of acid concentration and its high content overloads the resin, thus hindering the selective separation. Under proper conditions the copper matrices can be removed by precipitation, leaving the trace elements quantitatively in aqueous sample solution [8–10]. The detailed separation procedure is shown in Fig. 1.

In order to optimize the separation procedure a series of cold experiments were performed first. For this a set of solutions in 1 M HNO_3 with different copper content of 20, 50 and 100 mg/ml and analyte concentrations of 25 and 50 μg/ml, respectively, were prepared. Twenty milliliters of each solution were saturated with H_2S to precipitate CuS. After the precipitation the suspension was purged shortly with nitrogen and filtrated on a Nalgene 0.45 mm Bottle Top Filter. The filter was washed with hot water and aliquots are taken for copper analyses by ICP-OES. Further, the filtrate was evaporated and conditioned in as small as possible volume of 12 M HCl. The load solution was passed through an anion exchange column Dowex 1 × 8 (100 × 9 mm) preconditioned with 12 M HCl. At these conditions Al and Ni were not retained on the anion exchanger and were removed as a group with the load solution and following wash. Further the elements of interest were eluted consecutively with decreasing concentration of HCl. Manganese was eluted first with 10 M HCl, Ti with 8 M HCl followed by Co eluted with 4 M HCl. The residue of Cu was removed from the column with 2.5 M HCl and finally iron was eluted with 0.5 M HCl. The fraction containing Al and Ni was conditioned in 0.1 M HCl and loaded on Dowex 50 × 8 cation exchanger column. Then Ni was eluted with 0.5 M HCl and Al with 3 M HCl. Each fraction was collected for the concentration determination of the respective element by means of ICP-OES.

On the next step 50 mg of active copper material was dissolved in 7 M HNO_3 and stable copper solution was added to a final copper concentration of 20, 50 and 100 mg/ml, respectively in 1 M HNO_3. Each sample was spiked with 2.5 kBq ^{54}Mn. In this way prepared samples were separated following the above described procedure. The Mn, Ti and Co fractions were analyzed by gamma spectrometry. To study the distribution of Ni and Fe LSC was used to analyse ^{63}Ni and ^{55}Fe isotopes which are

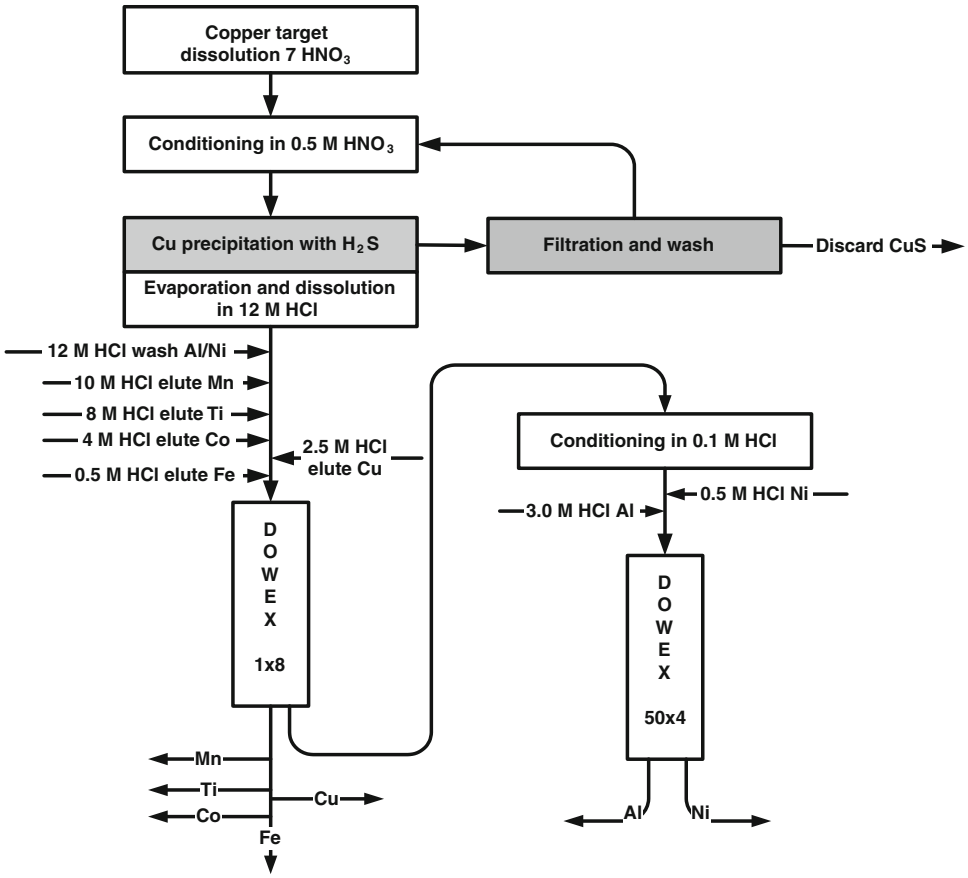

Fig. 1 Flowchart of the radiochemical separation procedure. The developed radiochemical separation procedure was used to create a remote controlled system for separation of exotic radionuclides from gram amounts of proton irradiated copper

present together with ^{59}Ni and ^{60}Fe in the sample. Due to the long half-life and low concentration, ^{26}Al distribution was evaluated only with a stable carrier.

Hot cell system for separation of exotic radionuclides

Based on the above described radiochemical separation procedure, a remote controlled system for separation of Al, Ni, Mn, Ti, Co and Fe was designed and installed in a modular four-compartments hot-cell. Each compartment is equipped with master-slave manipulator, separate ventilation system as well as inlets and outlets for liquids and gasses transportation. The separation system consists of two parts which are installed in two neighbouring hot-cell compartments. In the first part of the system the dissolution of the copper target, matrix precipitation and conditioning for the ion-exchange separation was done. In the second part of the system the ion-exchange separation of the elements was taking part, as well as conditioning and reduction of the volume of the liquid wastes.

Dissolution, precipitation and conditioning

The scheme of the remote controlled separation system—stage one, which includes dissolution of the material, copper precipitation as CuS and conditioning for ion-exchange, is shown in Fig. 2. The copper chips are dissolved in *Cu dissolution* vessel with in 7 M HNO_3. A stream of N_2 was used to purge out the NO_X gases and to stir the solution. After the copper material was completely dissolved, by means of a peristaltic pump and manifold distributive valves, Milli Q water was added to bring the solution to 0.5 M HNO_3. Next the conditioned solution was transported to the *CuS precipitation vessel* and saturated with H_2S. After the CuS precipitation the suspension was purged with N_2 in order to remove the residue of H_2S. Then the separation of CuS was done by a self-aspirating filter system in *CuS Filtration vessel*. The clear solution was directed to a *Rotavapor M* where it was prepared for ion-exchange. After the total volume of the clear solution was evaporated and conditioned in 8 M HCl it was transported to the second part of the separation system.

Ion-exchange separation and waste conditioning

In the second part of the system, Fig. 3, the ion-exchange separation was performed. Many parameters that play a key role for the good separation are difficult to be controlled in a hot-cell, such as capillary, valves and columns dead volumes, effective residue from the copper matrix etc. The

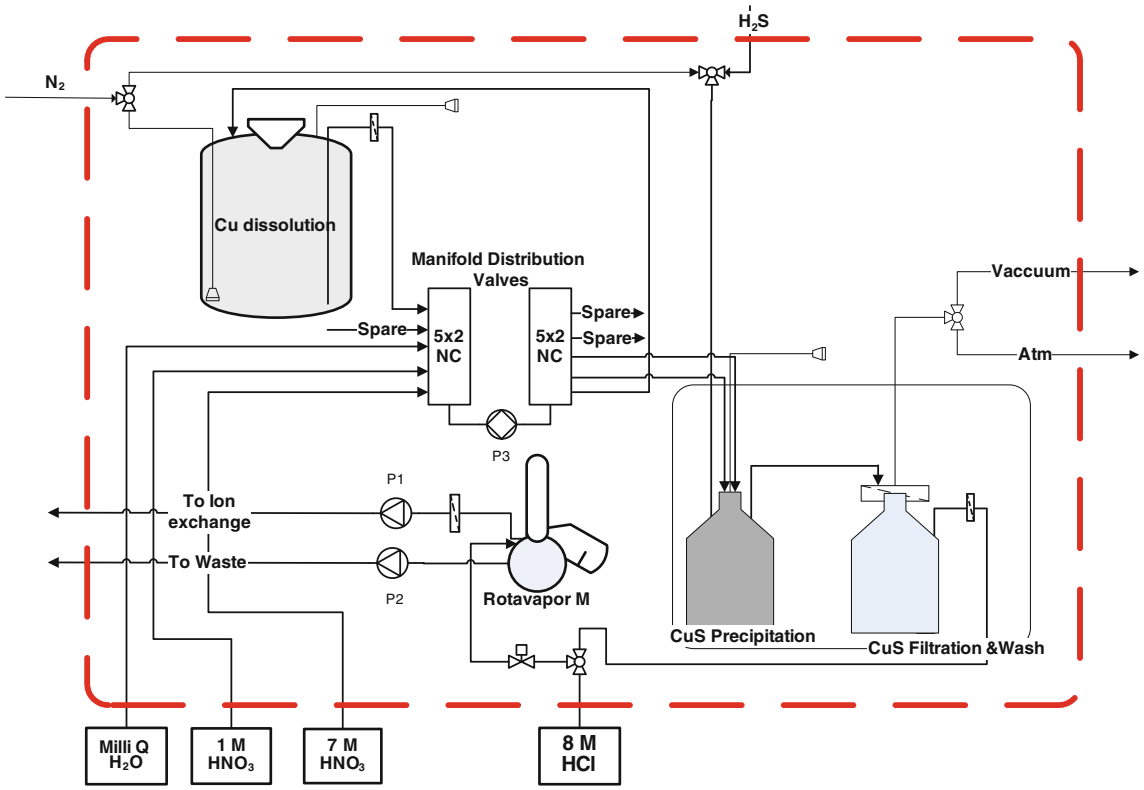

Fig. 2 Dissolution and precipitation part of the remote controlled separation system. * The components inside the *dash line* are installed in the hot-cell

use of highly concentrated acid solutions should be avoided in order to reduce the possibility of corrosion and damages to the hot-cell equipment. For this reason we altered the separation procedure. Instead of 12 M HCl, we chose 8 M HCl as a load solution. It was directed through one of the four possible ion-exchange columns, followed by wash with 8 M HCl.

The load and wash fractions were passing a gamma activity detector and were collected outside the hot-cell. In this way Ni, Al, Mn and Ti were removed from the hot-cell with the load and the column wash in a single fraction and separated from high ^{60}Co activity. In the next step Co was eluted with 4 M HCl and its fraction was collected in a receptacle vessel inside the hot-cell. The elution of ^{60}Co was monitored by a gamma detector. After cobalt was removed from the column, the remaining copper was eluted with 2.5 M HCl and collected as waste outside the hot-cell. Finally the iron fraction was eluted with 0.5 M HCl. At the end of the separation procedure the used ion-exchange columns were regenerated with 0.1 M HCl and conditioned with 12 m HCl for the next separation.

Waste management

The system embeds a ^{60}Co waste conditioning step. The cobalt fraction was diluted to 0.1 M HCl and retained on a disposable cation-exchange column—Dowex 50 × 8. After its saturation the column was removed from the hot-cell and disposed. This procedure not only decreases drastically the volume of the high activity ^{60}Co wastes, but also transforms them from liquid to solid form.

Final purification steps

Further the separation and purification of the respective fraction was implemented out of the hot-cell. To separate Al, Ni, Mn and Ti their fractions were conditioned in a volume of 1 to 2 ml 12 M HCl. The separation was performed on a 100 × 9 mm Dowex 1 × 8 column. Al and Ni were removed with the load solution and 5 ml wash. In the next step Mn was eluted with 25 ml 12 M HCl. Titanium was removed from the column with 30 ml 8 M HCl.

The fraction containing Al and Ni was conditioned in 0.1 M HCl and loaded on Dowex 50 × 8 cation exchange column (20 × 7 mm). Ni was eluted with 15 ml 0.5 M HCl followed by Al with 20 ml 3 M HCl.

The iron fraction conditioned in 6 M HCl was loaded on a Dowex 1 × 8 anion-exchange column (20 × 7 mm). Traces of ^{60}Co were eluted with 30 ml of 4 M HCl and then iron stripped from the column with 0.5 M HCl.

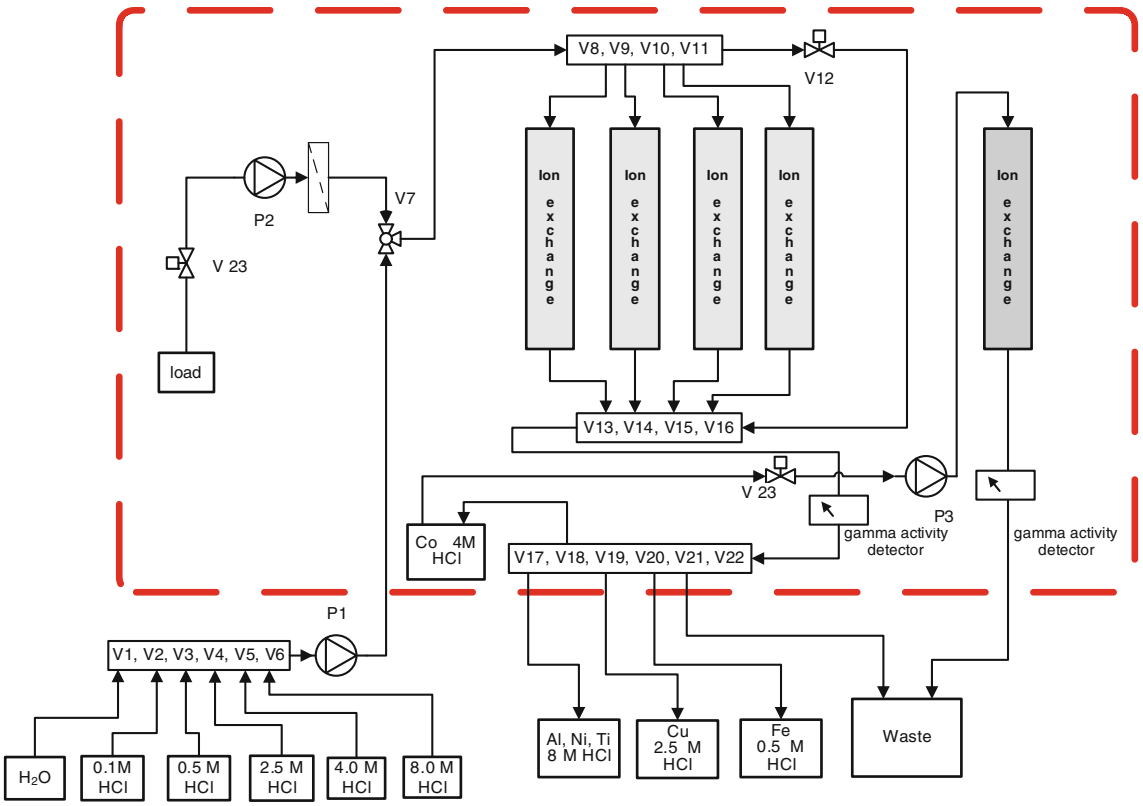

Fig. 3 Ion exchange part of the remote controlled separation system. * The components inside the *dash line* are installed in the hot-cell

Results and discussion

The results from the carrier-added experiment for the copper concentration before and after precipitation with H_2S revealed a separation factor in the range of 90,000. The copper matrix residue in the solution was less than a microgram per milliliter concentration. At the same time the losses of Al, Ni, Mn, Ti and Fe were negligible—lower than one percent.

In the second, no carrier-added experiment where the radionuclides were present at very low concentrations without carrier, we have observed analytes losses during the copper matrix precipitation Table 2. With increasing copper matrix concentrations analyte losses increase up to twenty percents.

Table 2 Recoveries of the non carrier-added radionuclides from the copper matrix precipitation

Isotope	Recovery from 20 mg/ml copper concentration, %	Recovery from 50 mg/ml copper concentration, %	Recovery from 100 mg/ml copper concentration, %
^{55}Fe	95	90	85
^{63}Ni	95	90	82
^{60}Co	95	91	80
^{54}Mn	98	95	90

This can be explained with an occlusion that was taking place even at the relatively high acid concentration of the solution at the precipitation step and it was in good agreement with the results of similar studies published earlier [9]. Multiple wash of the filter with hot water helps to improve the recovery of the rare isotopes. Residual copper was not interfering with the next step of ion-exchange separation. The composite elution profile of the elements of interest in the system Dowex 1 × 8—HCl is presented in the Fig. 4. The results are obtained by ICP-OES, gamma spectrometry and LSC.

The elution profile demonstrates that selective separation of the elements was achieved, though a tailing of Al/Ni fraction into the Mn one and the Mn fraction tailing into the Ti one was observed. Nevertheless that only small part of the ^{60}Co activity was tailed in the titanium fraction, due to its high specific activity it was comparable with the total titanium activity and interferes severely with further Ti application. To achieve a better decontamination of the exotic radionuclides from each other and from the main gamma impurity—^{60}Co, additional separation steps were applied.

The gamma spectra of the copper sample spiked with ^{54}Mn and the titanium fraction after the second purification step are presented in the Fig. 5. Before the separation the gamma spectrum was dominated by the ^{60}Co activity. After

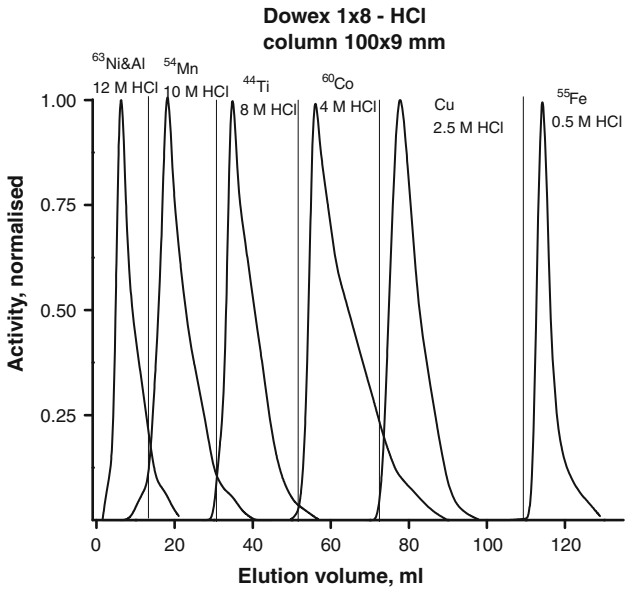

Fig. 4 Elution profile of Ni, Mn, Ti, Co, Cu and Fe from the system Dowex 1 × 8—HCl

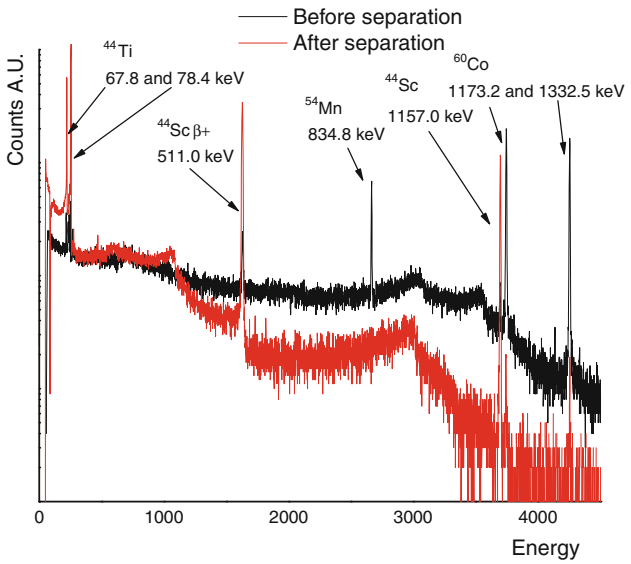

Fig. 5 The gamma spectra of the copper sample spiked with ^{54}Mn and the titanium fraction after the second purification step

purification the ^{60}Co activity was significantly reduced and a decontamination factor of 10^6 was achieved.

The remote controlled system for separation of exotic radionuclides from proton irradiated copper dump material was installed in a hot-cell and tested for reliability and of operation as well as for selectivity and chemical yield of the separation. During the test period c.a. 13.8 g of copper material were used for the separation of ^{26}Al, ^{59}Ni, ^{53}Mn, ^{44}Ti and ^{60}Fe. All radionuclides were separated in non carrier added form. In the Table 3 the overall yields separation of the separation procedure are presented.

Table 3 Overall yield of the separation procedure

Element	Recovery, %
Al	45
Ni	53
Mn	65
Ti	70
Fe	72

The yield of ^{26}Al is evaluated by use of stable Al tracer

Conclusions

The results demonstrated that the system was functional and reliable for remote handling of highly radioactive material. The separation of rare isotopes was achieved with satisfactory selectivity and yields for Mn, Ti and Fe. The procedure manages as well the generated liquid wastes containing high level of ^{60}Co activity, reducing significantly their volume. Yet the testing revealed some week points of the separation scheme. The recovery of Al and Ni was unsatisfactory and the substantial amount of ^{53}Mn is lost with Al/Ni fraction. In our opinion, further efforts are needed to improve the recovery of Al and Ni. To make the system fully operational, a work for the optimization of the selective copper matrix precipitation with H_2S is ongoing.

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